Wear of cryo-treated engineering polymers and composites

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Abstract

Polymers and composites are extensively used in wear situations dominated by various types of abrasive mechanisms. Incorporation of fillers and fibers, heat treatment and surface engineering by various chemical and physical techniques have been successfully employed to enhance wear behavior of metals as well as non-metals. In the case of metals, cryo-treatment is an emerging technique for improving wear resistance. However, this tool has not been applied for polymeric materials. Hence, in this paper investigations on the influence of cryo-treatment on wear performance of a series of thermoplastic engineering polymers such as Polyimide (PI), Polyetherimide (PEI), Polytetrafluoroethylene (PTFE), Polycarbonate (PC) and Polyurethane (PU) are presented. A series of composites of PI, PEI and its copolymer with increasing amount of short glass fiber and solid lubricants was also investigated. The selected materials were cryogenically treated at liquid nitrogen temperature for 24 h. Abrasive wear performance was evaluated at ambient temperature for a single pass on a pin-on-disc machine using Silicon Carbide (SiC) paper as a counterface. Comparison of wear rates of treated and untreated samples under various loads revealed that this technique has potential to increase the wear resistance of some polymers and composites. Fiber loading higher than 20%, however, showed deterioration in wear after cryo-treatment. The extent of influence of cryo-treatment on wear resistance depended on the type of base matrix and the nature and amount of fibre or particulate filler. Changes in crystallinity and hardness were studied and correlated with observed wear behavior. Scanning electron microscopy (SEM) was used to investigate changes in morphology due to cryo-treatment.

Keywords: Engineering polymer; Short fiber reinforcement; Abrasive wear resistance; Cryogenic treatment

1. Introduction

Performance of a tribo-component depends mainly on five factors, i.e., material, testing parameters, counterface, wear modes and their mechanisms [1]. Since bulk property requirements of the materials for each wear situation are quite diverse, no single material can exhibit the required performance in all types of wear situations. In the case of polymers, the wear performance of virgin polymer is not always very satisfactory and needs to be modified employing the following techniques.

(1) Control and design of bulk properties, e.g., molecular weight distribution, entanglement density, microstructure, crystallinity, etc. [2].

(2) Filler/Fiber reinforcement. However, the filler incorporation and fiber reinforcement done to improve the wear behavior of the base polymer for a particular application may not be beneficial for other wear situations. At times, it can worsen the performance [3,4].

(3) Development of an interpenetrating network (IPN) structure.

(4) Surface modifications by plasma treatment, ion implantation, photo polymerization, physical and chemical vapor deposition and silicone modification, etc [5,6].

All surface or bulk modification techniques are associated with certain advantages and limitations from applicability, extent of enhancement in a desired property and the economic point of view. In light of the above, efforts are being made to explore newer techniques for improving wear performance [7–9]. Cryogenic treatment (hereafter referred to as cryo-treatment) is comparatively a very simple tool for modifying the bulk properties of metals and is being reported as an emerging technique for enhancing
mechanical properties and the wear performance of metals significantly [10–13]. However, to the best of the authors’ knowledge, this technique has not been employed for enhancing the tribo-performance of polymers or composites. Since polymers and composites are extensively used for various abrasive wear applications [14], efforts need to be made to enhance their abrasive wear resistance.

In our earlier work on evaluating the wear performance of materials with proven potential in adhesive wear applications, it was concluded that such tribo-materials show poor wear resistance in severe sliding conditions, i.e., in the abrasive wear mode [3,4]. Most of the fiber reinforcements like glass fibers (GF), carbon fibers (CF) and fillers and solid lubricants such as Polytetrafluoroethylene (PTFE), MoS₂, graphite and bronze powder proved to be detrimental in this respect. However, in our recent work [15,16], it was claimed that short glass fiber reinforcement can also enhance wear performance of a neat polymer if it is in the right concentration (30% in the case of Polyetherimide (PEI)). Hence, it was thought worthwhile to explore the potential of cryo-treatment for improving the wear performance of polymers and composites including the ones mentioned above. Abrasive wear studies were done on treated and untreated materials in a single pass. These investigations are reported in the following sections.

2. Experimental

A series of PEI composites [15] was selected for cryo-treatment along with five composites of polyimide. A set of base matrices was selected on the basis of crystallinities and proven tribo-potential either in adhesive or in abrasive wear modes. PTFE (highly crystalline polymer) and its composites, which exhibit excellent performance in adhesive wear mode, were also selected. Polyurethane (PU) which is known as a very good abrasive wear resistant material was also selected for comparison. Polycarbonate (PC) was selected on the basis of its amorphous and brittle nature. Ultem (trade name for PEI) materials were supplied by GE Plastics, USA. Vespel (polyimide (PI) and its composites and carbon fiber reinforced PTFE (Zymax)

<p>| Table 1 |
|-------------------|---|---|---|---|
| Details of materials selected and their wear performance | | | | |</p>
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Designation</th>
<th>Material</th>
<th>²of short fibers/fillers</th>
<th>Abrasive wear performance</th>
<th>Approximate changes in Shore D hardness as compared to untreated sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>A₀</td>
<td>1000</td>
<td>-</td>
<td>30% increase</td>
<td>12% increase</td>
</tr>
<tr>
<td>2.</td>
<td>A₅₀</td>
<td>2100</td>
<td>10% GF</td>
<td>15% increase</td>
<td>7% increase</td>
</tr>
<tr>
<td>3.</td>
<td>A₅₀</td>
<td>2200</td>
<td>20% GF</td>
<td>2% increase</td>
<td>4% increase</td>
</tr>
<tr>
<td>4.</td>
<td>A₅₀</td>
<td>2300</td>
<td>30% GF</td>
<td>25% decrease</td>
<td>13% decrease</td>
</tr>
<tr>
<td>5.</td>
<td>A₅₀</td>
<td>2400</td>
<td>40% GF</td>
<td>35% decrease</td>
<td>16% decrease</td>
</tr>
<tr>
<td>6.</td>
<td>A₂₅GF + 15% + 15%MoS₂</td>
<td>4000</td>
<td>25% GF + 15% PTFE + 15% (Graphite + MoS₂)</td>
<td>5% increase</td>
<td>5% increase</td>
</tr>
<tr>
<td>7.</td>
<td>B₀</td>
<td>6000</td>
<td>-</td>
<td>2% increase</td>
<td>15% increase</td>
</tr>
<tr>
<td>8.</td>
<td>B₅₀</td>
<td>6100</td>
<td>10% GF</td>
<td>7% increase</td>
<td>8% increase</td>
</tr>
<tr>
<td>9.</td>
<td>B₅₀</td>
<td>6200</td>
<td>20% GF</td>
<td>3% decrease</td>
<td>18% decrease</td>
</tr>
<tr>
<td>10.</td>
<td>C₀</td>
<td>SF1</td>
<td>-</td>
<td>3% increase</td>
<td>8% increase</td>
</tr>
<tr>
<td>11.</td>
<td>C₂₅GF</td>
<td>SF21</td>
<td>15% Graphite</td>
<td>15% increase</td>
<td>15% increase</td>
</tr>
<tr>
<td>12.</td>
<td>C₄₀GF</td>
<td>SF22</td>
<td>40% GF</td>
<td>5% decrease</td>
<td>7% increase</td>
</tr>
<tr>
<td>13.</td>
<td>C₂₅GF + 15%</td>
<td>SF21</td>
<td>15% GF + 10% PTFE</td>
<td>5% increase</td>
<td>9% increase</td>
</tr>
<tr>
<td>14.</td>
<td>C₅₀</td>
<td>SF23</td>
<td>15% MoS₂</td>
<td>9% decrease</td>
<td>7% decrease</td>
</tr>
<tr>
<td>15.</td>
<td>D₀</td>
<td>-</td>
<td>-</td>
<td>60% increase</td>
<td>22% increase</td>
</tr>
<tr>
<td>16.</td>
<td>D₂₅GF</td>
<td>-</td>
<td>25% GF</td>
<td>13% increase</td>
<td>9% increase</td>
</tr>
<tr>
<td>17.</td>
<td>D₅₀₅₀ B + 5%MoS₂</td>
<td>-</td>
<td>55% B + 5%MoS₂</td>
<td>1% increase</td>
<td>5% increase</td>
</tr>
<tr>
<td>18.</td>
<td>D₂₂CF</td>
<td>-</td>
<td>25% short CF</td>
<td>40% increase</td>
<td>15% increase</td>
</tr>
<tr>
<td>19.</td>
<td>E</td>
<td>PC</td>
<td>-</td>
<td>13% increase</td>
<td>2% increase</td>
</tr>
<tr>
<td>20.</td>
<td>F</td>
<td>PU</td>
<td>-</td>
<td>11% increase</td>
<td>10% increase</td>
</tr>
</tbody>
</table>

²A comparison with untreated and cryo-treated materials. Load 14 N, Sic paper 80 grade, abraded distance 3 m and speed 5 cm/s.
B = Bronze, GF = short glass fiber, CF = short carbon fiber, T = PTFE, M = MoS₂ and grf = graphite.
Fig. 1. Comparative abrasive wear performance of untreated and cryo-treated polymers at 14 N load.

were procured from Dupont, USA. The other materials were procured from local suppliers. Materials were supplied either in the form of test bars or as rods from which square pins of size (1 cm x 1 cm x 0.3 cm) were cut for wear studies.

These samples were subjected to controlled cooling in a cryogenic chamber. Liquid nitrogen temperature (77 K) was attained in 8 h and the samples were kept for 24 h at that temperature. The samples were brought back to room temperature with a controlled heating rate at the rate of 35°C/h. Abrasive wear studies were carried out on the pin-on-disc machine discussed elsewhere [3]. Untreated and cryo-treated samples were initially abraded at a speed of 5 cm/s against very fine waterproof Silicon Carbide (SiC) polishing paper (grade 1200, grit size = 5 μm) for uniform contact. The pins were then cleaned with acetone, dried and weighed. These pins were slid against SiC paper of 80 grade (grit size = 176 μm) fixed on a rotating disc with a constant speed of 5 cm/s under different normal loads (6–14 N). After abrading for 3 m distance, for single pass the pins were cleaned with a brush to remove debris. Weight loss was measured and converted into volume loss by using density data. Repeatability of the results for the selected system was confirmed by conducting 10 tests on neat PEI sample. The readings were within 99.5% confidence level. Once the method was standardised, the tests were repeated three times for other samples and the average value was reported.

Fig. 2. (a) Influence of cryo-treatment on wear performance of A_{25GF+15T+15(M+gr)5} (ULTEM 4000). Influence of fibre concentration on abrasive wear performance of: (b) untreated and (c) cryo-treated. PEI composites at different loads (v = 5 cm/s, d = 3 m; abrasive paper 80 grade): A_{10} — PEI neat, A_{10} — PEI + 10% GF, A_{20} — PEI + 20% GF, A_{30} — PEI + 30% GF, A_{40} — PEI + 40% GF, A_{25GF+15T+15(M+gr)5} — 25%GF + 15% PTFE + 15% Graphite + MoS2).
Fig. 3. Influence of fiber concentration on abrasive wear performance of: untreated (a) and cryo-treated (b) PEI copolymer composites at different loads ($v = 5$ cm/s, $d = 3$ mm, abrasive paper 80 grade). $B_0$—PEI copolymer neat, $B_{10}$—PEI copolymer + 10% GF, $B_{20}$—PEI copolymer + 20% GF.

The following studies were carried out to understand the microstructural changes in the material due to cryo-treatment. X-ray diffraction studies were carried out on a Philips X-ray diffractometer for a few treated and untreated polymers to detect changes in crystallinity. Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA) were done for a few samples using a General V4.1C Dupont 2100 analyzer. Shore D hardness tests were carried out for selected samples to find out the changes in hardness due to cryo-treatment. Morphological

Fig. 4. Wear volume as a function of load for: (a) untreated and (b) cryo-treated polyimide (PI) composites ($v = 5$ cm/s, $d = 3$ mm, abrasive paper 80 grade). $C_0$—PI neat, $C_{15}g$—PI + 15% graphite, $C_{40}g$—PI + 40% graphite, $C_{15}g + 10T$—PI + 15% graphite + 10% PTFE, $C_{15}M$—PI + 15% MoS$_2$. 
and fiber-matrix interface studies were carried out for a few untreated and cryo-treated samples using Scanning Electron Microscopy (SEM).

3. Results and discussion

Table 1 lists trends in wear behavior modification. Abrasive wear data for untreated and cryo-treated samples are presented in Figs. 1–6. Fig. 1 shows comparative

Fig. 5. Wear volume as a function of load for: (a) untreated and (b) cryo-treated Polytetrafluoroethylene (PTFE) composites (v = 5 cm/s; d = 3 m; abrasive paper 80 grade). D_55B—PTFE neat, D_{25C}—PTFE + 25% graphite, D_{55B+25M}—PTFE + 55% Bronze + 25% MoS_2. D_{25CF}—PTFE + 25% CF.

Fig. 6. Wear volume as a function of load for untreated and cryo-treated PC and PU (v = 5 cm/s; d = 3 m; abrasive paper 80 grade). E—Poly carbonate (PC), F—Polyurethane (PU).

Fig. 7. X-ray diffractograms of: (a) (i) untreated and (ii) cryo-treated PEI, (b) (i) untreated and (ii) cryo-treated PTFE. (c) (i) untreated and (ii) cryo-treated PTFE.
abrasive wear performance of treated and untreated neat polymers selected in the studies. In Figs. 2 and 3, wear volume as a function of fiber concentration at various loads and temperatures is plotted while in Figs. 4 and 5, wear volumes at different loads are plotted for various PI and PTFE composites with different concentrations of fillers and solid lubricants. In Fig. 6, wear behavior of PC and PU is shown as a function of load. Fig. 7a–c shows X-ray diffraction of untreated and cryo-treated PEI, PI, and PTFE, respectively. Figs. 8–10 show DSC and TGA curves of PEI, PI, and PTFE while SEM micrographs are collected in Figs. 11 and 12.

From the results presented, the following are the salient observations:

Cryo-treatment has certainly indicated a potential to enhance the abrasive wear performance of the studied materials. However, the extent of improvement depended on the material and in the case of composites, it depended on the type of fillers and fibers also.

In the case of neat polymers, abrasive wear performance improved for all the polymers due to cryo-treatment.

Enhancement was maximum for PEI (≈ 30%) and PTFE (≈ 60%). For PI and PEI copolymer it was, however, small (≈ 2%). PC and PU showed moderate improvement (≈ 10–15%) due to cryo-treatment.

Increase in hardness due to cryo-treatment was found to be one of the prominent factors responsible for enhancement in wear performance of polymers and composites.

Cryo-treatment proved most effective in the case of composites containing PTFE and graphite. For MoS₂ and bronze powder improvement with this treatment was not significant while in the case of GF reinforcement it proved detrimental.

Cryo-treatment worked synergistically for a combination of fillers viz. PTFE and graphite.

In the case of PEI, DSC and TGA studies indicated changes in crystallinity due to cryo-treatment.

Fig. 8. DSC and TGA curves of: (a) untreated and (b) cryo-treated PEI.
XRD studies done for PEI and PI polymers also showed marginal increase in crystallinity due to cryo-treatment. However, XRD studies carried out for PTFE did not show any change.

The SEM was found to be useful in correlating wear performance with morphological changes due to cryo-treatment.

In the case of metals, improvement in hardness and hence, wear performance due to cryo-treatment has been reported [13]. In the present studies, a similar trend was observed in the case of selected polymers and composites also. Interestingly, polymers and composites, which showed improvement in their wear performance due to cryo-treatment, have also shown increase in hardness due to treatment. Hardness values, as seen in Table 1, are completely in accord with the wear performance (with the exception of C_{avg}). Lhynn’s mathematical model [17] for correlating abrasive wear rate with various material properties, is best suited under the present test conditions, since the abrating speed is low. The Lhynn’s equation indicates that hardness is inversely proportional to specific wear rate or directly proportional to abrasive wear performance.

Consequently, an increase in hardness should theoretically increase the abrasive wear performance and this was indeed observed in the case of the cryo-treated samples studied.

3.1. Wear studies on polymers

Fig. 1 shows comparative abrasive wear performance of treated and untreated neat polymers selected in the studies. In the case of neat polymers, crystallinity is generally in the order PTFE > PI > PU > PC > Copolymer of PEI > PEI. PTFE is almost 90% crystalline while PEI is 99% amorphous. Both polymers showed maximum enhancement in the performance due to cryo-treatment (Fig. 1). An increase in crystallinity due to cryo-treatment has been reported to be responsible for enhancement in wear performance of metals [13]. A similar possibility could not be ruled out in the case of polymers also. Hence, X-ray diffraction studies were also done on PEI, PI and PTFE polymers. A marginal increase in crystallinity was observed only in the case of PI and PEI as seen in Fig. 7a.
Fig. 10. DSC and TGA curves of: (a) untreated and (b) cryo-treated PTFE.

and b respectively. DSC and TGA studies also showed supporting trends. DSC curves of untreated and cryo-treated samples of PEI (Fig. 8a, b) indicated that the glass transition temperature ($T_g$) increased from 215.30°C to 252.91°C which indicated an increase in crystallinity. However, in the case of PI, which is a crystalline polymer, the $T_g$ criterion does not hold good. A distinct DSC exothermic peak starting from 99°C in the case of cryo-treated PI (Fig. 9b) could not be due to trapped moisture since any form of water in materials is indicated by an endothermic peak. Moreover, a TGA curve for cryo-treated PI did not show any weight loss around 100°C (Fig. 9b). This typical peak in DSC around 99°C and a weight loss peak around 300°C (only in the case of cryo-treated PI) could not be satisfactorily explained. Perhaps, non-uniformity in the crystalline regions in the original sample resulted in more alignment due to cryo-treatment. In the case of PTFE, hardly any change in crystallinity was expected since PTFE as such is crystalline (99%) polymer. DSC curves of untreated and cryo-treated PTFE showed marginal changes in crystallinity while TGA curves appeared to be almost unchanged (Fig. 10a, b). The reason behind enhancement in the performance of cryo-treated PTFE thus was thought to be mainly due to an increase in hardness rather than an increase in crystallinity due to treatment. An additional experiment was done to confirm whether some additional mechanisms were responsible for the observed behavior. SEM studies were performed on treated and untreated PTFE powder (Fig. 11a, b) instead of pins. In the case of untreated powder (Fig. 11a), particles were observed to be quite separated from each other. However, cryo-treated particles were found to be agglomerated (Fig. 11b). A very dense network of microfibrils originating from each particle was a remarkable and distinct feature of treated powder (Fig. 11d). Such microfibrils were rarely seen in the case of untreated powder (Fig. 11c). This typical behavior of agglomeration and excessive fibrillation of PTFE powder (Fig. 11d) due to treatment could be caused by the following: PTFE is the only polymer which shows ductile behavior (about 1%) even at 4 K and this is due to its unique
molecular structure consisting of fluorine groups arranged in a spiral [18]. When the sample is taken from 77 K to ambient temperature, fibrillation took place. This is clearly seen in micrograph (Fig. 11d) whereas very little fibrillar structure was observed in untreated PTFE polymer (Fig. 11c). Fig. 12a shows a micrograph of a clean, untreated PEI surface, whereas a micrograph of cryo-treated PEI surface is shown in Fig. 12b. The surface texture of the untreated polymer appeared to be quite smooth compared to the rough topography of the cryo-treated surface. The enhanced roughness of the surface could be due to the contraction at cryogenic temperatures and uneven expansion when it was brought back to the ambient temperature. The residual stresses developed in the polymer owing to the difference in temperature and residual strains developed due to the contraction force might have been responsible for these topography changes.

3.2. Wear studies on composites

Wear vs fiber content plots showing minima at 30% GF loading for untreated PEI composites (Fig. 2b) have been already discussed in detail in our earlier work [15,16]. As seen in Fig. 1 and Table 1, cryo-treatment increased the wear performance of PEI approximately by 30%. In the case of GF composites, however, different trends were observed. Performance of composite (30% GF) was best in the case of untreated series and worst in the case of treated series. Extent of improvement due to treatment was maximum in the case of neat PEI and 10% GF. Beyond 20% loading, overall wear resistance reduced very fast confirming that cryo-treatment is not beneficial for short glass fiber reinforced composites with GF higher than 10%. Ineffectiveness of cryo-treatment in the case of composites including PEI copolymer composites (with the exception of B10) (Fig. 3) was attributed to the fact that when composites are subjected to liquid nitrogen temperature, differential contraction takes place between fibre and matrix leading to matrix–fiber interfacial debonding. This effect becomes more pronounced as fiber concentration increases. Large internal stresses do get generated when material undergoes thermal shock. It is reported in the literature [19] that in the case of an Al/SiC composite, quenching in liquid nitrogen followed by heating to room temperature generated compressive residual stresses of about 25 MPa compared to a tensile stress of 50 MPa resulting from heating and cooling back to room temperature. Withers et al. [20] reported the change in axial strains in both fiber and matrix during cyclic thermal shock of
short fiber composites. Stress relaxation processes vary with the type of matrix, the fiber length and the severity of thermal shock. When stress relaxation cannot occur easily, and if the matrix is relatively brittle, then matrix microcracking is likely. Hence, it was essential to investigate microstructural changes in GF reinforced PEI composite due to cryo-treatment. Instead of using a plain surface, the edges of composites were scanned using SEM since the probability of fibers protruding from the matrix is always high along the cut edges. Surfaces of untreated and treated PEI (A40) composites are shown in micrographs 12c and 12d at the same magnification. Increase in space between fibers and matrix due to cryo-treatment indicated deterioration in fiber-matrix bonding (Fig. 12d). Micrograph 12e is for a cryo-treated surface of a composite A40. A fiber-tip microcut into pieces due to cryo-treatment is seen on the surface. Fiber microcutting and fiber-matrix debonding due to treatment leading to reduction in hardness were
observed to be prominent factors responsible for deterioration in the wear performance of short GF reinforced composites.

Particulate fillers viz. graphite and PTFE have shown a very interesting trend in cryo-treated samples. In all the composites, these fillers have enhanced the wear performance due to cryo-treatment (except C_{15sfr}) very significantly. In fact, a synergistic effect was observed when PTFE and graphite were incorporated as fillers in the case of C_{15sfr}. In the case of MoS_{2} and bronze, however, negligible improvement was seen.

It was also thought worthwhile to study the influence of cryo-treatment on samples, which were cut into the required pin shape after cryo-treatment. Abrasive wear studies of such samples did not show any improvement in wear performance. This could be due to the mechanical stresses induced in the samples while cutting and machining, nullifying beneficial effects due to cryo-treatment. Hence, it was concluded that for beneficial performance, finished components should be cryo-treated only at the final stage.

4. Conclusions

In this paper, investigations on the effectiveness of cryo-treatment on the wear performance of polymers and composites have been reported. The cryogenic treatment has proved to be an effective technique enhancing abrasive wear performance. The potential of the treatment, however, depended upon the particulate fillers, fiber reinforcement and their combinations and the polymers selected, i.e., PEI, PI, PTFE, PU and PC. Among the selected polymers, maximum enhancement in wear performance was seen in the case of PTFE followed by PEI. It was also seen that this technique should not be used for short glass fiber reinforced composites. Increase in hardness due to cryo-treatment was found to be the most important parameter responsible for performance enhancement. X-ray diffraction studies on treated and untreated polymers indicated an increase in crystallinity of amorphous and semi-crystalline polymers due to treatment resulting in enhancement of wear performance. Cryo-treatment of composites containing PTFE and graphite fillers was found to be the most effective. It was also concluded that cryo-treatment is effective for the finished components only.

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References